AN IMPROVED METHOD FOR THE ESTIMATION OF NITRATES IN WATER BY MEANS OF THE PHENOLSULPHONIC ACID REACTION.

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SPRENGEL'S method of estimating nitrates by means of the reaction with phenolsulphonic acid is probably that most frequently utilised in water analysis. The process is to evaporate 10 to 25 c.c. of the sample to dryness on the steam bath, and to treat the residue with 2 c.c. of phenolsulphonic acid; the whole is taken up with water, rendered alkaline with 20 c.c. of strong ammonia or potassium hydroxide solution, and made to a definite volume. The yellow colour of the nitro compound produced with nitrates is compared with that from a standard solution of potassium nitrate, and, by appropriate dilution and matching of the colours, the quantity of nitrogen as nitrates present in the sample is deduced. To prepare 1 litre of the phenolsulphonic acid reagent, 132 grms. of pure phenol is mixed with 60 c.c. of ammonia-free distilled water, and 815 c.c. of concentrated nitrogen-free sulphuric acid is added; the mixture is heated at 80 to 85° C. for six hours.

While it is well known that the presence of chlorides in the sample causes loss of nitrogen, it is perhaps not generally realised that the under-estimation is so great as to render the process inapplicable as a general method. The determination has been the subject of research by the writer, and a method which eliminates error has been evolved.

Effect of Chlorides on Sprengel's Method.

Solutions of potassium nitrate were prepared each containing 0·4 parts nitrogen as nitrate and varying amounts of sodium chloride as shown below. These were examined for nitrates by Sprengel's method, and the following results were obtained:

Cl per 100,000.	Nitrogen as Nitrates Found, per 100,000.	Percentage Error.
2·4	0·40	Nil.
9·2	0·35	−12·5
18·0	0·31	−22·5
30·0	0·27	−32·5
48·0	0·22	−45·0
60·0	0·18	−55·0
80·0	0·16	−60 0
100·0	0·16	−60·0

All natural waters contain chlorides, and the unreliability of the method is evident from the foregoing figures.

Effect of Addition of Phenolsulphonic Acid before Evaporation.

Some two years ago the writer tried the modification of adding the phenolsulphonic acid *before* evaporation and evaporating until all the water removable by steam heat was evaporated as shown by the residual acid liquid assuming a dark colour, a condition which may be conveniently termed here as "acid dryness." It was found that while the error due to chlorides was, to some extent, reduced, there was a persistent and irregular over-estimation A series of sample solutions similar to the above, examined by this modification and compared with average "standards," gave the results undernoted:

Cl per 100,000.	Nitrogen as Nitrates Found, per 100,000.	Percentage Error.
2·4	0 42	+ 5·0
9·2	0·42	+ 5·0
18·0	0·42	+ 5·0
30·0	0·49	+22·5
48·0	0·55	+37·5
60·0	0·44	+10·0
80·0	0·42	+ 5·0
100·0	0·47	+17·5

Effect of Addition of a Diluted Phenolsulphonic and Sulphuric Acid Mixture.

The quantity of reagent employed in Sprengel's method is enormously in excess of that required to react with 25 c.c of samples rarely containing more than 4·0 parts nitrogen as nitrates per 100,000. This was confirmed in practice by obtaining complete reaction with 0·08 c.c. of phenolsulphonic acid added to 25 c.c. of a solution of potassium nitrate of the above strength.

In view of this a phenolsulphonic acid solution was prepared by heating only 4 grms. of phenol with 25 c.c. of concentrated sulphuric acid and making to 1 litre. Two c.c. of this solution, added previous to evaporation, reacted completely with 25 c.c. of solutions of potassium nitrate containing nitrogen up to 4·0 parts per 100,000; but with natural waters reaction was incomplete, as the residue failed to remain liquid owing to the increased quantity of solid matter present. It was eventually found necessary, in order to make the solution effective for general use, to increase the sulphuric acid to 400 c.c. per litre; the amount of phenol remained unaltered.

Twenty-five c.c. of solutions of potassium nitrate, each containing 0·4 parts nitrogen as nitrates per 100,000, without chlorides, and with chlorides varying from 2·4 to 100 parts Cl per 100,000, were treated with 2 c.c. of the reagent before evaporation to "acid dryness," taken up with water, rendered alkaline with 3 c.c. of strong ammonia, and made to 100 c.c. The colours obtained in the final solutions varied with a maximum difference of only ± 5 per cent., and the solutions containing chlorides did not vary to a greater degree than those without, showing elimination of the error due to the presence of chlorides.

With a view to obtaining more thorough interaction between the nitrates and phenolsulphonic acid, a similar series was treated with the acid as above. In this series each water contained 0·4 parts nitrogen as nitrates per 100,000, four portions were without chlorides, and eight others contained 3·2, 10, 20, 30, 40, 60, 80, and 100 parts Cl per 100,000 respectively. The "acid dryness" residue was taken up with 5 to 10 c.c. of ammonia-free water, mixed, and again evaporated; this process of solution and evaporation to "acid dryness" was repeated. The residue was taken up with water and made alkaline as before. The colourations obtained were all equal, indicating that in this modification the nitrate value obtained was constant even in the presence of chlorides up to 100 parts of Cl per 100,000.

Further experiments were made to determine whether the colour intensity obtained in the final solution is proportionate to the amount of nitrate originally present. Samples of water were prepared containing 0·08, 0·2, 0·3, and 0·8 parts of nitrogen as nitrates associated with 40, 30, 20, and 40 parts of chlorine as chlorides per 100,000 respectively, and were examined by the final modification of the process. It was found that the intensity of the colours obtained with the prepared samples was in proportion to the amount of nitrate, showing that the colour varies directly with the nitrate present. In addition these results show that the method gives accurate determinations of nitrates in the presence of large and varying amounts of chlorine.

The accuracy of this process has been confirmed by examination of excessively hard waters containing large amounts of chlorides and (comparatively) high nitrates.

It has been noted when using the diluted phenolsulphonic acid and sulphuric acid mixture that the colour of the final solution is much more pure and brilliant than that obtained by the original method, this greatly facilitates accurate matching with the standards.

Detailed Process.

SOLUTIONS REQUIRED: *Standard Potassium Nitrate Solution.*—1·4434 grms. of pure KNO_3 per litre, 25 c.c. = 5·0 mgrms. N as nitrates; this solution is diluted 1 in 50, then 25 c.c. = 0·1 mgrm. N as nitrates.

Phenolsulphonic-Sulphuric Acid Mixture.—4 grms. of phenol (Calvert's No. 1 is very suitable) is mixed with 4 c.c. of ammonia-free distilled water and 100 c.c. of concentrated nitrogen-free sulphuric acid is added; the whole is heated at 80 to 85° C. for 6 hours, cooled, and made to 500 c.c. Three hundred c.c. of concentrated nitrogen-free sulphuric acid made to 500 c.c. with ammonia-free distilled water is added and mixed with the foregoing solution to give one litre of reagent

METHOD.—Spherical-bottomed, 3½ inches diameter, porcelain basins are used each containing a small glass rod. To one basin 25 c.c. of the sample is added, and to the other 25 c.c. of the dilute standard potassium nitrate solution. Two c.c. of the phenolsulphonic-sulphuric acid mixture is added to each and thoroughly mixed by stirring. Both are evaporated on the steam bath until no more water is expelled ("acid dryness"), and the residual liquid assumes a dark colour. During the progress of the evaporation the liquid is occasionally stirred, and any dark spots on the side of the basin above the surface of the liquid are incorporated in the bulk of the residue by touching with the glass rod. The basins are then removed from the steam bath, and, by gently tilting them and directing the liquid with the rod, the residue is made to come in contact with all parts of the inside of the basin. All material on the sides of the basin is washed to the bottom with a very fine jet of ammonia-free distilled water; the 5 to 10 c.c. required is mixed with the bulk by stirring, and the whole is again evaporated to "acid dryness." The residue is once more taken up with water and evaporated to "acid dryness" as already described.

The final residues are taken up with water and poured into thin, colourless, measuring glasses, and the basins are washed out with small quantities of water to about 95 c.c.; 3 c.c. of strong ammonia (sp. gr., 0·880) is added and the whole made to 100 c.c. The contents of each glass are separately mixed by placing the palm of the hand tightly on the open end of the glass and inverting four or five times; to prevent loss of liquid, one edge of the lip of the glass is pressed tightly against the palm in withdrawing. The colour obtained in each glass is proportionate in intensity to the quantity of nitrate originally present.

A solution of potassium hydroxide may be used in place of ammonia, but is only satisfactory when prepared the same day. The colour obtained with a sample must always be compared with a standard prepared by the same process. In the few cases where the quantity of nitrogen as nitrates in a sample approximates or exceeds 4 parts per 100,000, the determination is repeated using only 10 c.c. of the sample; in the last 500 samples analysed by the writer, received from every kind of supply in all parts of the United Kingdom, this quantity has only been exceeded three times.

The advantages of this process may be summarised:

1. Nitrogen as nitrates, associated with chlorides up to 100 parts chlorine per 100,000, is accurately estimated.

2. The purity of the colours obtained in the final solutions makes matching easy.

3. The large saving of reagents is a consideration. Calculating on 2 c.c. of phenolsulphonic acid and 20 c.c. of ammonia used in the original process, there is a saving of 97 per cent. of phenol, 50 per cent. of sulphuric acid, and 85 per cent. of ammonia.

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